CLAIMS

1. A process for the preparation of a polymerizable dental composition comprising the steps of

(a) preparing a liquid mixture comprising

(i) 1 to 99% w/w of a hybrid monomer component containing at least one hybrid monomer compound having one hydrolysable siloxane group and at least one polymerizable organic moiety, and

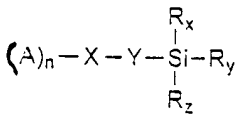
(ii) 99 to 1% w/w of a monomer component polymerizable with the polymerizable organic moiety of the hybrid monomer compounds; and

(b) adding at least a stoichiometrically sufficient amount of water to the mixture to hydrolyse the hydrolysable siloxane group of the hybrid monomer compound and to form spherical polymerizable nanoparticles having an average particle size of from 1 to 100 nm dispersed in the monomer component, whereby the nanoparticles have a structure with Si-O-Si bonds and peripherally exposed polymerizable organic moieties.

2. The process according to claim 1, wherein nanoparticles have an average particle size of from 1 to 20 nm.

3. The process according to claim 1, wherein nanoparticles have an average particle size of from 1 to 5 nm.

4. The process according to claim 1, wherein the hybrid monomer compound is a compound of the following formula (I)



wherein

A is a polymerizable moiety, preferably an acrylate or methacrylate group;

R_x, R_y, R_z

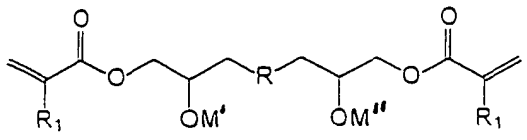
which may be the same or different independently represent substituted or unsubstituted C_1 to C_{18} alkoxy, C_5 to C_{18} cycloalkoxy, a C_5 to C_{15} aryloxy, C_2 to C_{18} acyloxy or halogen;

X is a nitrogen atom or a substituted or unsubstituted C_1 to C_{18} alkylene, C_1 to C_{18} oxyalkylene or C_1 to C_{18} carboxyalkylene group;

Y is a substituted or unsubstituted C_1 to C_{18} alkylene, C_1 to C_{18} oxyalkylene, C_5 to C_{18} cycloalkylene, C_5 to C_{18} oxycycloalkylene, C_5 to C_{15} arylene, or C_5 to C_{15} oxyarylene or heteroarylene group; and

n is an integer of 1 to 10.

5. The process according to claim 1, wherein the hybrid monomer compound is a compound of the following formulas 1-10:



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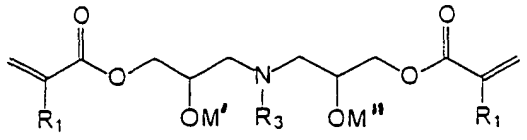

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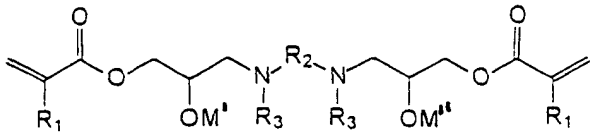

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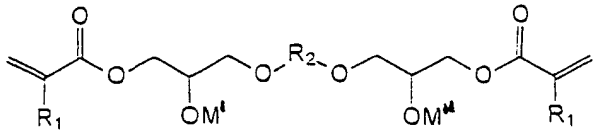

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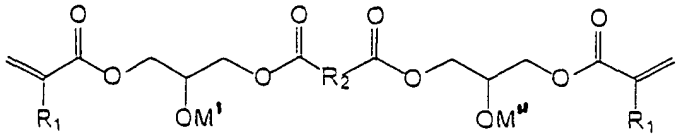

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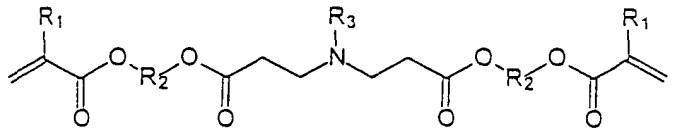

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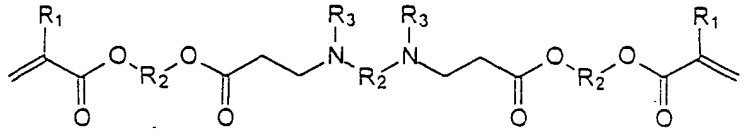

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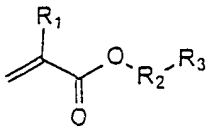

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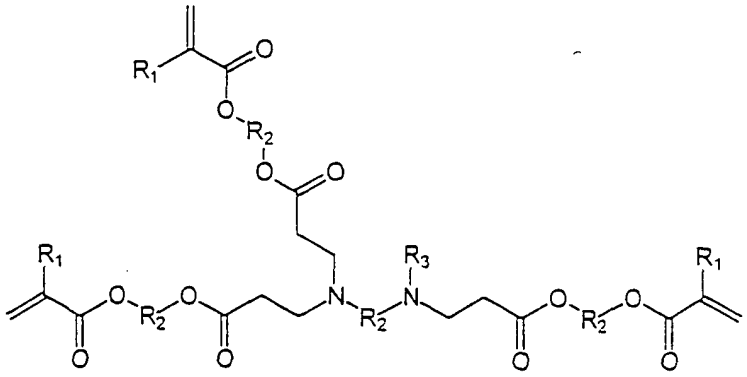

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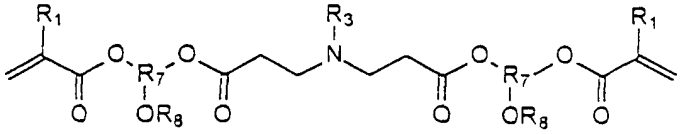

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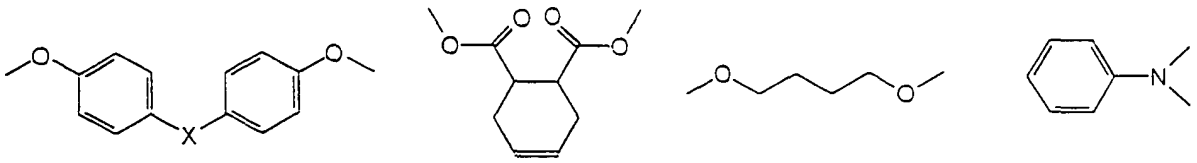
wherein

R is a residue derived from a diepoxide, notably a residue of the following formula

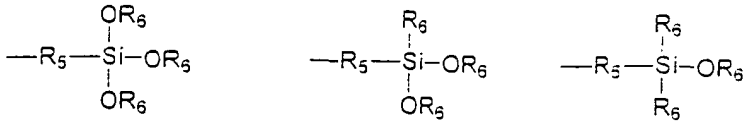


wherein X is $C(CH_3)_2$, $-CH_2-$, -O-, -S-, -CO-, or $-SO_2-$;

R_1 is hydrogen or a substituted or unsubstituted C_1 to C_{18} alkyl, C_5 to C_{18} cycloalkyl, C_5 to C_{18} aryl or heteroaryl group;

R_2 is a divalent substituted or unsubstituted C_1 to C_{18} alkylene, C_2 to C_{12} alkenylene, C_5 to C_{18} cycloalkylene, C_5 to C_{18} arylene or heteroarylene,

R_3 which may represent the same or different substituents in formula **3** and **7**, is a substituted or unsubstituted C_1 to C_{18} alkyl, C_2 to C_{12} alkenyl, C_5 to C_{18} cycloalkyl, C_6 to C_{12} aryl or C_7 to C_{12} aralkyl group, or a siloxane moiety represented by one of the following formulae I, II or III



I II III

wherein

R_5 is a divalent substituted or unsubstituted C_1 to C_{18} alkylene, C_2 to C_{12} alkenylene, C_5 to C_{18} cycloalkylene, C_5 to C_{18} arylene or heteroarylene group, preferably $CH_2CH_2CH_2$,

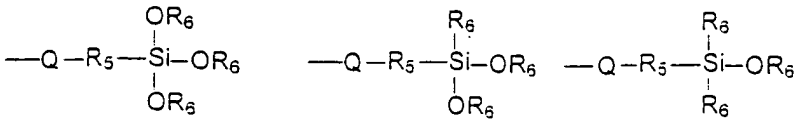
R_6 is a substituted or unsubstituted C_1 to C_{18} alkyl, C_2 to C_{12} alkenyl, C_5 to C_{18} cycloalkyl, C_6 to C_{12} aryl or C_7 to C_{12} aralkyl group,

R_7 is a substituted or unsubstituted C_1 to C_{18} alkylene, C_2 to C_{12} alkenyl, C_5 to C_{18} cycloalkylene, C_5 to C_{18} arylene or heteroarylene group,

R_8 is a protecting group for a hydroxyl group, preferably forming an ether, an ester or an urethane group,

M' and M"

which may represent the same or different substituents, is a siloxane moiety represented by one of the following formulae IV, V or VI, a protecting group for a hydroxyl group, preferably forming an ether, an ester or an urethane group, or hydrogen in case R_3 is a siloxane moiety represented by one of formulae I, II, or III as defined above,



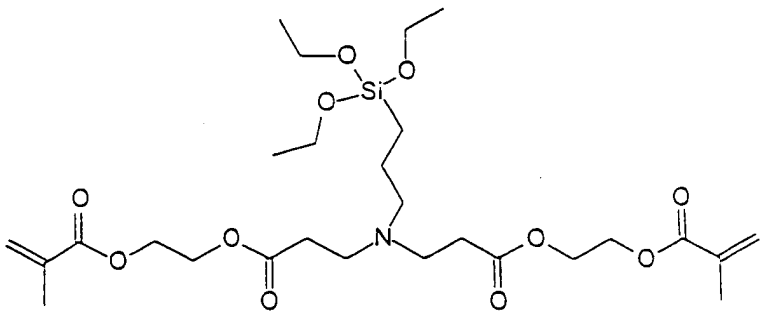
IV V IV

wherein

Q is an ether, an ester, a urethane or thiourethane linking group, and

R_5 and R_6 are as defined above.

6. The process according to claim 1, wherein the hybrid monomer component comprises a compound of the following formula **11** or **12**:



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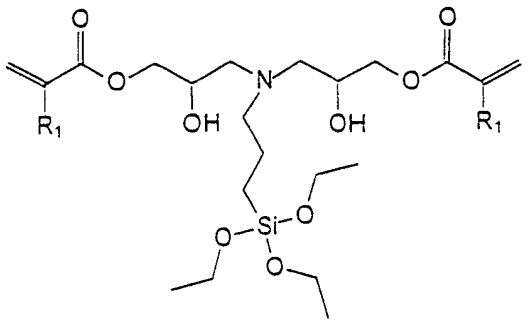

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7. The process according to claim 1, wherein said polymerizable monomer is a mono- or polyfunctional acrylate or methacrylate, selected from the group of methyl methacrylate, ethyleneglycol dimethacrylate diethyleneglycol dimethacrylate triethyleneglycol dimethacrylate, 3,(4),8,(9)-dimethacryloyloxymethyltricyclodecane, dioxolan bismethacrylate, vinyl-, vinylen- or vinyliden-, acrylic- or methacrylic substituted spiroorthoesters, spiroorthocarbonates or bicyloorthoesters, glycerin trimethacrylate, trimethylol propane triacrylate, furfurylmethacrylate.

8. The process according to claim 1, wherein the nanoparticles are formed in the presence of metal compounds selected from the group of alkoxides or metal complexes such as metal acetyl acetonates whereby the metals are selected from the group of Ba, Al, La, Ti, Zr, Tl, In or other transition elements or elements of the lanthanides or actinides.

9. The process according to claim 1, further comprising the step of adding an inorganic filler selected from La_2O_3, ZrO_2, $BiPO_4$, $CaWO_4$, $BaWO_4$, SrF_2,

Bi_2O_3, a porous glass or an organic filler, such as polymer granulate, embrittled glass fibres or a combination of organic and/or inorganic fillers or reactive inorganic fillers.

10. The process according to claim 1, further comprising the step of adding a polymerisation initiator and a stabiliser.

11. The process according to claim 1, wherein hydrolysis is carried out in the presence of a catalyst.

12. The process according to claim 12, wherein the catalyst is an acid or base.

13. The process according to claim 1, wherein hydrolysis is carried out under neutral conditions.

14. The process according to claim 1, wherein the composition comprises a polymerizable di- or poly(meth)acrylate, at least a polymerizable monomer, polymerisation initiators and/or sensitisers and stabilisers.

15. The process according to claim 1, wherein hydrolysis is carried out in the presence of an organic solvent such as THF, dioxane, chloroform, toluene, acetone.

16. The process according to claim 1, wherein hydrolysis is carried out in the presence of polymerizable monomers such as methyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, trimethylol propane triacrylate, 3,(4),8,(9)-dimethacryloyloxymethyltricyclo decane, dioxolan bismethacrylate, glycerol trimethacrylate, furfuryl methacrylate.

17. A polymerizable dental composition obtainable according to the process of any one of claim 1.